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<p>(54) Title: METHOD FOR THE PREPARATION OF A CATALYST SUITABLE FOR THE POLYMERISATION OF AN OLEFINE</p> <p>(57) Abstract</p> <p>The invention relates to a method for the preparation of a catalyst suitable for the polymerisation of an olefine by: a) bringing metallic magnesium into contact with a compound RX, R being an aromatic, aliphatic or cycloaliphatic group containing 1 to 20 carbon atoms and X being a halogen, and then b) bringing the obtained reaction product (I) into contact with an alkoxide and a Ti-containing compound, characterised in that an aromatic halogenide is used as the compound RX, an alkoxysilane-containing compound as the alkoxide and TiCl₄ as the Ti-containing compound.</p>		

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METHOD FOR THE PREPARATION OF A CATALYST
SUITABLE FOR THE POLYMERISATION OF AN OLEFINE

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The invention relates to a method for the preparation of a catalyst suitable for the polymerisation of an olefine by

- 10 a) bringing metallic magnesium into contact with a compound RX, R being an aromatic, aliphatic or cycloaliphatic group containing 1 to 20 carbon atoms and X being a halogen, and then
- 15 b) bringing the obtained reaction product I into contact with an alkoxide and a Ti-containing compound.

Such a method is known from EP-A-0,425,702, which describes that a catalyst is prepared by

a) bringing metallic magnesium into contact with a

20 halogen-containing compound having a formula RX, R being a hydrocarbon group containing 1 to 20 carbon atoms and X being a halogen. Then the reaction product is brought into contact with a compound that satisfies the formula:

- $$X^1_n M(OR^1)_{m-n},$$
- 25 X^1 being hydrogen, a halogen or a hydrocarbon group containing 1-20 carbon atoms, M being boron, carbon, aluminium, silicon or phosphorus, R^1 being a hydrocarbon group containing 1-20 carbon atoms, m having the valency of M, and $m > n \geq 0$, and a titanium alkoxide having the
- 30 formula $Ti(OR^2)_4$, R^2 being a hydrocarbon group containing 1 to 12 carbon atoms.

A drawback of the method for the preparation of the catalyst described above is that it is necessary to activate the catalyst obtained by successively carrying

35 out a prepolymerisation step and adding an electron donor and a titanium compound.

The aim of the invention is to obtain a method for the preparation of the catalyst which obviates this need to activate the catalyst.

The invention is characterised in that an
5 aromatic halogenide is used as the compound RX, an
alkoxysilane-containing compound as the alkoxide and TiCl_4
as the Ti-containing compound.

In this way a very active catalyst for the
polymerisation of an olefine is obtained without the need
10 to perform additional activation steps.

A further advantage of the catalyst according to
the invention is that there is no need to wash out the
catalyst after the polymerisation of an olefine.

From EP-A-0,319,227 a method is known for the
15 production of a catalyst suitable for the polymerisation
of an olefine by:

- a) bringing metallic magnesium into contact with a
compound RX, R being an aromatic, aliphatic or
cycloaliphatic group containing 1 to 20 carbon atoms and X
20 being a halogen and an alkoxide
and then
- b) bringing the magnesium-containing solid reaction
product into contact with a halogen-containing alcohol and
then with
- 25 c) an electron donor and a Ti-containing compound. The
method described above yields a catalyst that is less
active than the catalyst obtained with the method
according to the invention.

Preferably, the method according to the
30 invention is carried out by first bringing reaction
product I into contact with the alkoxysilane-containing
compound, after which the precipitate formed is worked up
into a reaction product II that is then
c) brought into contact with TiCl_4 .

35 In this way it is possible to control the morphology of
the catalyst particles and hence of the polymer powder
obtained by using the catalyst.

With particular preference an electron donor is present in step c. In this way highly isotactic polypropylene is prepared during the polymerisation of propylene using the catalyst thus obtained.

5 Step a) of the method for the preparation of the catalyst according to the invention is carried out by bringing metallic magnesium and a compound RX into contact with one another.

All forms of metallic magnesium may be used as the
10 metallic magnesium, but preferably use is made of magnesium powder or magnesium chips. To obtain a fast reaction it is preferable to heat the magnesium under nitrogen before use. Aromatic halogenides are used as the compound RX, R being an aromatic group containing 6 to 18
15 carbon atoms and X preferably being chlorine or bromine. Chlorobenzene, bromobenzene and iodine benzene can be mentioned as examples.

Preferably chlorobenzene is used as the compound RX.

The magnesium and the compound RX are brought
20 into contact with one another in the presence of an inert solvent, for example an aliphatic, alicyclic or aromatic solvent containing 4-10 carbon atoms. Preferably an ether is used as the solvent, for example diethyl ether, diisopropyl ether, dibutyl ether, diisobutyl ether,
25 diisoamyl ether, diallyl ether, tetrahydrofuran (THF) or anisole. With particular preference dibutyl ether is used as the solvent. The aromatic halogenide/solvent ratio is important with respect to obtaining an active catalyst. The chlorobenzene/dibutyl ether volume ratio may for
30 example vary between 75:25 and 35:65. The best results are obtained when the volume ratio is between 70:30 and 50:50. When the ratio drops below 35:65 the bulk density of the polyolefine powder prepared with the aid of the catalyst is too low and when the ratio exceeds 75:25 the activity
35 of the catalyst according to the invention becomes too low.

Small amounts of iodine and/or alkyl halides can be added

to cause reaction a) to proceed at a higher rate.
Examples of alkyl halides are butyl chloride, butyl
bromide and 1,2-dibromoethane.

Reaction a) is carried out with stirring, but it is
5 important that not too much turbulence occurs. In the case
of a high degree of turbulence, the catalyst will show a
wide particle size distribution and the particle size
distribution of the polyolefine obtained with the catalyst
will also be wide. The reaction temperature is between 20
10 and 150°C; the reaction time between 0.5 and 10 hours.

During step b) of the reaction, reaction product
I, obtained after step a) of the reaction, is brought into
contact with an alkoxysilane-containing compound and
TiCl₄.

15 The following examples of alkoxysilane-containing
compounds can be mentioned: tetramethoxysilane,
tetraethoxysilane, tetrabutoxysilane,
tetraisobutoxysilane, tetraphenoxysilane, tetra(p-
methylphenoxy)silane, tetrabenzoyloxysilane,
20 methyltrimethoxysilane, methyltriethoxysilane,
methyltributoxysilane, methyltriphenoxysilane,
methyltriphenoxysilane, ethyltriethoxysilane,
ethyltriisobutoxysilane, ethyltriphenoxysilane,
butyltrimethoxysilane, butyltriethoxysilane,
25 butyltributoxysilane, butyltriphenoxysilane,
isobutyltriisobutoxysilane, vinyl triethoxysilane,
allyltrimethoxysilane, phenyltrimethoxysilane,
phenyltriethoxysilane, benzyltriphenoxysilane,
methyltriallyloxysilane, dimethyldimethoxysilane,
30 dimethyldiethoxysilane, dimethyldiisopropoxysilane,
dimethyldibutoxysilane, dimethyldihexyloxysilane,
dimethyldiphenoxysilane, diethyldiethoxysilane,
diethyldiisobutoxysilane, diethyldiphenoxysilane,
dibutyldiisopropoxysilane, dibutyldibutoxysilane,
35 dibutyldiphenoxysilane, diisobutyldiethoxysilane,
diisobutyldiisobutoxysilane, diphenyldimethoxysilane,
diphenyldiethoxysilane, diphenyldibutoxysilane,

dibenzyl-diethoxysilane, divinyl diphenoxysilane, diallyldipropoxysilane, diphenyldiallylsilane, methylphenyldimethoxysilane and chlorophenyldiethoxysilane.

5 Preferably use is made of tetraethoxysilane.

Reaction product I can be brought into contact with the alkoxysilane-containing compound and TiCl_4 by

1. simultaneously bringing the alkoxysilane-containing compound and the TiCl_4 into contact with reaction
10 product I or
2. first bringing the alkoxysilane-containing compound into contact with reaction product I in step b) and then bringing reaction product II of step b) into contact with TiCl_4 in a step c).

15 Preferably method 2 is used.

Preferably an electron donor is also present in step c). Examples of electron donors are carboxylic acids, carboxylic anhydrides, esters of carboxylic acids, halogen
carboxylic acids, alcohols, ethers, ketones, amines,
20 amides, nitriles, aldehydes, alcoholates, phosphorus compounds, arsenic compounds and antimony compounds that are bound to organic compounds via carbon or oxygen, sulphonamides, thioethers, thioesters, organic silicon compounds and compounds containing a heteroatom, such as
25 nitrogen, sulphur, oxygen and phosphorus. Examples of carboxylic acids are methanoic acid, ethanoic acid, propanoic acid, butanoic acid, isobutanoic acid, acrylic acid, methacrylic acid, maleic acid, fumaric acid, tartaric acid, cyclohexanoic monocarboxylic acid, cis-1,2-
30 cyclohexanoic dicarboxylic acid, phenylcarboxylic acid, toluenecarboxylic acid, naphthalene carboxylic acid, phthalic acid, isophthalic acid, terephthalic acid and trimellitic acid.

The anhydrides of the aforementioned carboxylic acids can
35 be mentioned as examples of carboxylic anhydrides.

Examples of esters of carboxylic acids that can be mentioned are the mono- or polyvalent esters of the

above carboxylic acids, such as butyl formate, ethyl acetate, butyl acetate, ethyl acrylate, methacrylate, isobutyl methacrylate, methylbenzoate, ethylbenzoate, methyl-p-toluate, ethyl- α -naphthoate, monomethyl phthalate, dibutyl phthalate, diisobutyl phthalate, diallyl phthalate and diphenyl phthalate.

Examples of halogen carboxylic acids that can be mentioned are the halides of the above carboxylic acids, such as acetyl chloride, acetyl bromide, propyl chloride, butyl chloride, butyl iodide, benzyl bromide, p-toluyyl chloride and phthaloyl dichloride. Examples of alcohols are methanol, ethanol, butanol, isobutanol, xlenol and benzyl alcohol. Examples of ethers are diethyl ether, dibutyl ether, diisoamyl ether, anisole and ethylphenyl ether.

Examples of organic silicon compounds are: tetramethoxysilane, tetraethoxysilane, methyltrimethoxysilane, methyltributoxysilane, ethyltriethoxysilane, phenyltriethoxysilane and diethyldiphenoxysilane.

Examples of compounds containing a heteroatom are 2,2,6,6-tetramethylpiperidine, 2,6-dimethylpiperidine, 2-methylpyridine, 4-methylpyridine, imidazole, benzonitrile, aniline, diethylamine, dibutyl amine, thiophenol, 2-methylthiophene, isopropyl mercaptan, diethylthioether, diphenylthioether, tetrahydrofuran, dioxane, dimethylether, diethylether, anisole, acetone, triphenylphosphine, triphenylphosphite, diethylphosphate and diphenylphosphate.

Preferably dibutyl phthalate is used as the electron donor.

Preferably reaction product I is brought into contact with the alkoxysilane-containing compound and TiCl_4 in the presence of an inert hydrocarbon solvent, as described in step a). The optimum temperature for the addition of the alkoxysilane-containing compound to reaction product I is 0-5°C.

The Si/Mg molar ratio during step b) may vary from 0.1 to

1.5. Preferably the Si/Mg molar ratio is between 0.4 and 1.0.

The TiCl_4/Mg molar ratio during step b) or step c) may vary between 10 and 100. Preferably this ratio is between 10 and 50.

The molar ratio of the electron donor, if used, relative to the magnesium in step c) may vary between 0.05 and 0.75. Preferably this molar ratio is between 0.1 and 0.4. The reaction temperature during step c) is preferably 110-120°C. At higher or lower temperatures the activity of the catalyst according to the invention decreases.

The catalyst according to the invention is suitable for the preparation of polyolefines by polymerising an olefine in the presence of the catalyst and an organometallic compound containing a metal from any one of groups 1, 2, 12 or 13 of the Periodic System of the Elements (Handbook of Chemistry and Physics, 70th Edition, CRC Press, 1989-1990). Preferably the organometallic compound is an organoaluminium compound. As the organoaluminium compound use is made of compounds having the formula $\text{R}_n\text{AlX}_{3-n}$, R being an alkyl group or an aryl group and $1 \leq n \leq 3$. Examples of organoaluminium compounds are trimethylaluminium, triethyl aluminium, dimethylaluminium chloride, diethyl aluminium chloride, diethyl aluminium iodide, diisobutyl aluminium chloride, methylaluminium dichloride, ethyl aluminium dichloride, ethyl aluminium dibromide, isobutyl aluminium dichloride, ethyl aluminium sesquichloride, dimethylaluminium methoxide, diethyl aluminium phenoxide, dimethylaluminium hydride and diethyl aluminium hydride. An electron donor may also be present during the polymerisation of an olefine. Examples of possible electron donors have been described above with relation to the execution of step c) of the preparation of the catalyst. Preferably an alkoxysilane is used as the electron donor during the polymerisation. The molar ratio of Al relative to Ti during the polymerisation may vary from 0.1 to 2000. Preferably this ratio is between 5 and

300. The concentration of the electron donor in the polymerisation mixture is between 0.5 and 5 mol/l. The catalyst is suitable for the polymerisation of mono- and di-olefines containing 2 to 10 carbon atoms, such as ethylene, propylene, butylene, hexene and octene and mixtures thereof. The catalyst is particularly suitable for the polymerisation of propylene and mixtures of propylene and ethylene.

The polymerisation can be carried out in the gas phase or in the liquid phase. In the case of polymerisation in the liquid phase a dispersing agent is present, such as n-butane, isobutane, n-pentane, isopentane, hexane, heptane, octane, cyclohexane, benzene, toluene or xylene. Liquid olefine can also be used as a dispersing agent. The polymerisation temperature is usually between 0°C and 120°C, preferably it is between 40°C and 100°C.

The pressure during the polymerisation is usually between 0.1 and 6 MPa. The molecular weight of the polyolefine that is formed during the polymerisation is controlled by adding hydrogen during the polymerisation or any other agent known to be suitable for that purpose.

The polymerisation can be carried out in continuous mode or batchwise, under the normal polymerisation conditions. The polymerisation can be carried out in several, successive steps. The polymerisation can also be carried out by first effecting the polymerisation in the liquid phase and then in the gas phase.

The invention will be further elucidated with reference to the examples without being limited hereto.

Example I

Preparation of reaction product I

A three-necked flask, fitted with a reflux condenser and a funnel, was filled with magnesium powder (26 g, 1.07 mol). The flask was brought under nitrogen. The magnesium was heated at 80°C for 1 hour, after which a mixture of dibutyl ether (173 ml) and chlorobenzene (80

ml) was added. Then iodine (0.03 g) and n-chlorobutane (3 ml) were successively added to the reaction mixture. After the colour of the iodine had disappeared, the temperature was raised to 97°C and chlorobenzene (250 ml) was slowly added in 2.5 hours. The dark reaction mixture that was formed in the process was stirred for another 8 hours at 97°C. Then the stirring and heating were stopped and solid substance was allowed to settle for 48 hours. By decanting the solution above the precipitate, which contained reaction product I, a solution with a concentration of 1 mol/l of the soluble reaction product I was obtained. This solution was used in the further catalyst preparation.

15 Preparation of reaction product II

The solution of reaction product I (100 ml, 1 M) was dosed to a reactor. This solution was cooled to 0°C and a mixture of tetraethoxysilane (TES) (11.2 ml) and dibutyl ether (38 ml) was added, with stirring, in 2 hours.

After the solution had been added the reaction mixture was kept at 0°C for another 0.5 hour, with stirring, after which the temperature was raised to 60°C. Then the reaction mixture was kept at 60°C for 1 hour, after which the stirring was stopped and the solid substance was allowed to settle in 30 minutes. The supernatant was removed by decanting. The solid substance was rinsed five times using 150 ml of heptane. A pale yellow solid substance, reaction product II (13.5 g), was obtained, suspended in 40 ml of heptane.

Preparation of the catalyst

A reactor was brought under nitrogen and 300 ml of titanium tetrachloride, a slurry, containing 12 g of reaction product II in 36 ml of heptane, and dibutyl phthalate (7.2 ml) were dosed to it. Then the reaction mixture was heated to 115°C and stirred at this

temperature for 2 hours. Then the stirring was stopped and solid substance was allowed to settle for 30 minutes. The supernatant was removed by decanting, after which a mixture of titanium tetrachloride (150 ml) and
5 chlorobenzene (150 ml) was added. The reaction mixture was again heated to 115°C and stirred for 30 min., after which the solid substance was allowed to settle for 30 minutes. This last cycle was repeated one more time. The solid substance obtained was rinsed five times using 300 ml of
10 heptane of 60°C, after which the catalyst, suspended in heptane, was obtained.

Polymerisation of propylene

(1) A stainless steel polymerisation reactor was
15 inertised with the aid of nitrogen and was then filled with dry heptane free of oxygen (290 ml). Then triethyl aluminium (TEA) (1.2 mmol as a solution in 5 ml of hexane), phenyltriethoxysilane (0.06 mmol as a solution in 5 ml of hexane) and catalyst (0.01 g as a slurry in 1 ml
20 of hexane) were dosed. Furthermore 55 ml of hydrogen was dosed and propylene was dosed until a pressure of 0.2 MPa was reached. The reactor was then quickly brought to polymerisation conditions, with stirring: temperature 70°C, pressure 0.5 MPa. The polymerisation was then
25 allowed to take place under said conditions for 2 hours. Then the pressure was reduced to atmospheric pressure. The reactor contents were drained, after which the powder was separated from the heptane. The polypropylene powder was now dried further in a vacuum drying stove. 67.3 g of
30 polypropylene powder was obtained (see Table 1).

Example II

The catalyst was prepared as described in Example I. Propylene polymerisation was carried out in a
35 stainless steel reactor that was inertised with the aid of nitrogen and was then filled with dry n-heptane free of oxygen (5.5 l). Then 8 mmol of TEA, 0.4 mmol of

phenyltriethoxysilane and 0.071 g of catalyst were added as a slurry in 5 ml of n-heptane. Then the reactor was heated to 70°C. Propylene containing 2 vol.% hydrogen was dosed until a pressure of 0.8 MPa was reached for 2 hours.
5 1065 g of polypropylene powder was obtained (see Table 1).

Example III

Preparation of reaction product I

Reaction product I was prepared as described in
10 Example I, only diisoamyl ether was used as a solvent instead of dibutyl ether.

Preparation of reaction product II

Reaction product II was prepared as described in
15 Example I, only the tetraethoxysilane was added to the reactor in 70 minutes instead of in 2 hours.
14.2 g of reaction product II was obtained.

Preparation of the catalyst

20 The catalyst was prepared as described in Example I, only 150 ml of titanium tetrachloride plus 150 ml of chlorobenzene were added to the reactor instead of 300 ml of titanium tetrachloride and the reaction mixture was kept at 115°C for 1 hour instead of 2 hours.

25

Polymerisation of propylene

Propylene was polymerised as described in Example I (see Table 1).

30 Example IV

Preparation of reaction product I

Reaction product I was prepared as described in Example I, only 42 g of magnesium powder was used instead of 26 g of magnesium powder and the reaction with
35 chlorobenzene was carried out at 110°C instead of at 97°C. The solution obtained contained 0.67 mol/l of reaction product I.

Preparation of reaction product II

Reaction product II was prepared as described in Example I, only the tetraethoxysilane was added to the reactor in 80 minutes instead of in 2 hours.

5

Preparation of the catalyst

The catalyst was prepared as described in Example I.

10 Polymerisation of propylene

The polymerisation of propylene was carried out as described in Example I (see Table 1).

Example V15 Preparation of the catalyst

The catalyst was prepared as described in Example IV.

Polymerisation of propylene

20 Propylene was polymerised in the gas phase. The polymerisation was carried out in a stainless steel reactor at a constant propylene pressure and a constant temperature of 70°C, in the presence of hydrogen. 0.8 mmol of TEA as a solution in 7 ml of n-hexane, 0.04 mmol of
25 phenyltriethoxysilane as a solution in 7 ml of n-hexane, 0.012 g of catalyst as a slurry in 1 ml of n-hexane and 55 ml of hydrogen were dosed to the reactor, after which gaseous propylene was dosed until a pressure of 1.5 atmosphere was reached. All this was carried out at a
30 temperature of 40°C. Then the temperature was raised to 70°C and the propylene pressure to 5 atmosphere. The polymerisation took place for 2 hours, after which 86.4 g of polypropylene powder was obtained (see Table 1).

35

Comparative Experiment APreparation of reaction product I

Reaction product I was prepared as described in Example I, after which the solid substance and the solution of reaction product I were not separated.

Preparation of reaction product II

Reaction product II was prepared as described in Example I, using the mixture of the solid substance and the solution of reaction product I as reaction product I (100 ml of slurry, 0.2 mol Mg). 23.1 g of product A was obtained.

Preparation of the catalyst and the polymerisation of propylene

They were carried out as described in Example I (see the Table).

Comparative Experiment BPreparation of the catalyst

Reaction product II was prepared in the same way as described above in Example I. Then reaction product II was brought into contact with 2,2,2-trichloroethanol as follows: a slurry of reaction product II (6.3 g) in heptane (50 ml) was introduced, under nitrogen, into a three-necked flask (300 ml) fitted with a reflux condenser, a stirrer and a dropping funnel. This slurry was stirred at room temperature and 2,2,2-trichloroethanol (2.0 ml, 0.02 mmol) dissolved in n-heptane (11 ml) was added in 30 minutes. After all the alcohol had been added, the total reaction mixture was stirred for one hour at 80°C. Then the solid substance was removed through filtration and was rinsed four times, at room temperature, using n-hexane (100 ml per time) and twice using toluene (100 ml per time). The final product was then treated with titanium tetrachloride and electron donor in the manner described above for the preparation of the catalyst in

Example I.

Polymerisation of propylene

Finally, a polymerisation was carried out with
5 this product as described above for the polymerisation of
propylene in Example I (see Table 1).

Comparative Experiment CPreparation of reaction product II

10 Reaction product II was prepared as follows: a
three-necked flask, fitted with a reflux condenser and a
funnel, was filled with magnesium powder (6 g, 0.25 mol).
The flask was brought under nitrogen, after which the
magnesium was heated at 80°C for 1 hour. Then 42.4 ml of
15 dibutyl ether (0.25 mol), 55.8 ml of tetraethoxysilane
(0.25 mol), 15 ml of chlorobenzene, 2 ml of n-chlorobutane
and 0.02 g of iodine were dosed.
Then the mixture was stirred at 80°C until the colour of
the iodine disappeared, after which the mixture was heated
20 to 120°C and 70 ml of chlorobenzene was added in 2 hours,
after which the stirring was continued for another 4 hours
at 120°C. The stirring was stopped and the solid substance
was allowed to settle in 30 minutes. The supernatant was
removed by decanting. The precipitate was rinsed four
25 times using n-heptane (250 ml) of 60°C. Reaction product
II was obtained, suspended in heptane.

The preparation of the catalyst

The catalyst was prepared as described in
30 Example I, using the reaction product II obtained in the
above reaction as reaction product II.

Polymerisation of propylene

Propylene was polymerised as described in
35 Example I, using the catalyst prepared as described above.

Table 1: Polymerisation results

5

10

Example	CY		APP	II	BD	d50	span
	kg of PP/g of cat	kg of PP/g of Ti	(wt%)	(wt%)	(kg/m ³)	(μ m)	(d90-d10)/ d50
1	6.8	309	1.0	98.4	0.42	250	0.5
2	15.1	686	1.0	97.8	0.42	325	0.5
3	6.4	246	0.9	97.2	0.36	950	1.5
4	8.1	289	1.2	97.8	0.37	1180	1.4
5	7.2	257	-	96.1	0.37	1160	1.4
A	4.8	267	1.6	97.2	0.32	280	1.8
B	6.7	279	1.0	98.5	0.41	260	0.5
C	4.1	227	1.4	96.8	0.38	425	3.3

15 Measuring methods:

- The catalyst yield (CY) is the number of kg of propylene powder obtained per g of catalyst or per g of Ti.
- The weight percentage of atactic polypropylene (APP) was determined as follows:
250 ml of the filtrate (y ml) obtained in separating the polypropylene powder (x g) and the hexane was dried over a steam bath and then under a vacuum at 60°C. That yielded z g of APP.
The total amount of APP (q g) is: $(y/250)*z$.
The weight percentage of APP is: $(q/(q+x))*100\%$.
- The isotacticity index (II) of the polypropylene powder was determined as follows: 5 g of polypropylene powder was extracted with the aid of n-heptane in a Soxhlet extractor for 4 hours. The weight percentage of the polypropylene powder that does not dissolve in n-heptane is the isotacticity index.

30

- The bulk density of the polypropylene powder (BD) was determined according to ASTM D 1895.
- The d50 and the span were determined according to ASTM D1921, method A.

C L A I M S

1. Method for the preparation of a catalyst suitable for
5 the polymerisation of an olefine by
 - a) bringing metallic magnesium into contact with a compound RX, R being an aromatic, aliphatic or cycloaliphatic group containing 1 to 20 carbon atoms and X being a halogen
 - 10 and then
 - b) bringing the obtained reaction product I into contact with an alkoxide and a Ti-containing compound,
characterised in that an aromatic halogenide is used
15 as the compound RX, an alkoxysilane-containing compound as the alkoxide and TiCl_4 as the Ti-containing compound.
2. Method according to Claim 1, characterised in that
20 reaction product I is brought into contact with an alkoxysilane-containing compound, after which the precipitate formed is worked up into reaction product II that is subsequently
 - c) brought into contact with TiCl_4 .
3. Method according to Claim 2, characterised in that an
25 electron donor is also present in step c.
4. Method according to Claim 3, characterised in that the molar ratio of the electron donor relative to the magnesium in step c) is 0.1-0.4.
5. Method according to Claim 3 or Claim 4, characterised
30 in that the electron donor is dibutyl phthalate.
6. Method according to any one of Claims 1-5, characterised in that the aromatic halogenide is phenylchloride.
7. Method according to any one of Claims 1-6,
35 characterised in that the alkoxysilane-containing compound is tetraethoxysilane.

8. Method according to any one of Claims 1-7,
characterised in that the molar ratio of Si relative
to the magnesium in step b) is 0.4-1.0.
- 5 9. Method according to any one of Claims 1-8,
characterised in that the molar ratio of TiCl_4
relative to the magnesium in step b) or step c) is
10-50.
- 10 10. Method according to any one of claims 1-9,
characterised in that the temperature during step c)
is 110-120°C.
11. Catalyst obtainable with the aid of the method
according to any one of Claims 1-10.
12. Polyolefine prepared in the presence of a catalyst
according to Claim 11 and an organoaluminium
15 compound.
13. Propylene homo- and copolymer prepared in the
presence of a catalyst according to Claim 11 and an
organoaluminium compound.
- 20 14. Propylene homo- and copolymer prepared in the
presence of a catalyst according to claim 11, an
organoaluminium compound and an electron donor.

INTERNATIONAL SEARCH REPORT

Inter- national Application No
PCT/NL 95/00132A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08F10/00 C08F4/658

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	FR,A,2 392 038 (MONTEDISON) 22 December 1978 see page 19; example 4 see page 18; example 3 see page 10, line 22 - line 30 see page 11, line 1 - line 22 see page 11, line 27 - line 38 see page 12, line 9 see page 12, line 28 - line 31	1-4,7,8, 11-14
X	see page 2, line 34 - page 3, line 13	3
X	see page 5, line 4 - line 6	3
X	see page 5, line 12 - line 17 ---	4
A	EP,A,0 440 813 (TONEN CORPORATION) 14 August 1991 see claim 1 see page 8; example 4 ---	1

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☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents :

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- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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- *&* document member of the same patent family

Date of the actual completion of the international search

8 December 1995

Date of mailing of the international search report

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Fischer, B

INTERNATIONAL SEARCH REPORT

Inter PCT/NL 95/00132	nal Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 206 817 (SUMITOMO CHEMICAL COMPANY) 30 December 1986 see example 1 see page 7, column 23 -----	1,6

INTERNATIONAL SEARCH REPORT

...formation on patent family members

International Application No

PCT/NL 95/00132

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